

# COMPETITIVE HYDROGENATION OF MODEL HETEROCYCLES AND OF POLYNUCLEAR AROMATICS

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Comparison of hydrodesulfurization catalysts is generally complicated by the presence of diffusion effects and by the problems associated with laboratory trickle bed reactors (1). The importance of diffusion is underscored by the numerous patents and publications dealing with effects of pore size distribution (2), diffusivity (3), and porosity (4). Contacting effectiveness in trickle bed reactors was recently reviewed both in terms of liquid hold-up and of catalyst wetting characteristics (5).

In order to eliminate the effects of diffusion and of reactor design and to examine the chemistry and the relative rates of the reactions associated with commercial hydrodesulfurization, conversion of a series of model feed mixtures was studied over a conventional CoMo catalyst (6). Components of the feeds were chosen to be representative of the various chemical types found in petroleum, in shale oils, in coal oils, and the like. For sulfur species, sulfides and fused ring thiophenes were studied (7); for nitrogen, quinolines and indoles (8,9); and for oxygen, phenols, fused ring furans, and carboxylic acids (8,10).

For a conventional CoMo catalyst (6) it was found that NSO compounds could be grouped by chemical type, both with respect to the relative rates and to the mechanisms of heteroatom removal. More important, the behavior experienced with these model feed mixtures closely paralleled that known for actual heavy petroleum charge stocks. The hydrogen consumed in the "hydrodesulfurization" of coal oils, shale oils, and petroleum residua could be estimated from their heteroatom content and from the mechanistic data provided by the models.

In the following pages, these phenomenological studies on model feeds are extended to other catalysts, to NiMo as well as CoMo, to Mo-only catalysts. Again a comparison is drawn between the behavior of model feeds and that observed with actual charge stocks.

## Experimental

Four catalysts were used in these experiments and are described in Table I. All were commercial samples, HDS-2 (CoMo, American Cyanamid), HDS-1441 (SiO<sub>2</sub>-stabilized CoMo, Amer. Cyanamid), HDS-3 (NiMo, Amer. Cyanamid), and Mo-1201T (Mo-only, Harshaw). Each was sized to 60/80 mesh for testing.

Details of the hydrogenation apparatus, a high-pressure trickle bed reactor, were given earlier (6). Presulfiding was at 180°C, 2 hours, in a 20% H<sub>2</sub>S in H<sub>2</sub> stream. Reaction conditions were 344°C, 700 psig, WHSV=2, H<sub>2</sub>/feed=8. (~6500 SCF/bbl.)

Table I

Selected Hydrodesulfurization Catalysts

Catalyst	<u>HDS-2</u>	<u>HDS-1441</u>	<u>HDS-3</u>	<u>Mo-1201T</u>
Weight Percent				
CoO	4.5	2.8	-	<0.1
NiO	<0.1	-	2.8	-
MoO <sub>3</sub>	12.7	10.3	12.2	10.1
SiO <sub>2</sub>	<0.1	4.9	-	0.0
Surface Area, m <sup>2</sup> /g	280	280	190	150
Pore Volume, cc/g	0.58	0.57	0.60	0.37
Part. Density, g/cc	1.15	1.13	1.09	1.48
Real Density, g/cc	3.40	3.19	3.15	3.29
Pore Diam., Å	82	83	128	98
Pore Distribution (N <sub>2</sub> ), %				
<25Å radius	18	17	7	13
25-50	27	32	13	21
50-100	19	27	19	22
100-200	12	16	23	13
200-300	3	2	10	4
>300	21	6	27	27

Table II

Feed Compositions

Standard feed:	<u>Moles</u>	<u>Weight Percent</u>
Dibenzothiophene	1.0	10.4
Dibutylsulfide	1.0	8.2
Quinoline	1.0	7.3
Dibenzofuran	1.0	9.5
Naphthalene	1.0	7.2
2-Methylnaphthalene	2.0	16.0
2,3-Dimethylnaphthalene	1.0	8.8
Hexadecane	1.5	19.1
1,2,4-Trimethylbenzene	2.0	13.5
Substitute components:		
Benzothiophene	p-Cresol	
Indole	4-Propylphenol	
2,3-Benzofuran	2-Ethylphenol	
2-Phenylphenol		

Both elemental and gas chromatographic analyses were obtained on all samples, as described earlier (6). Hydrogen consumption values were calculated from elemental analysis.

## Results

Rate data. The feed compositions are detailed in Table II and represent an attempt to simulate the chemical composition of petroleum-type charge stocks while maintaining equimolar ratios of individual reactants. The standard feed contained 3.61% sulfur, 0.79% nitrogen, 0.90% oxygen, 8.79% hydrogen and 85.91% carbon. In general, only one feed component was changed at a time when comparing the relative rates and mechanisms of heteroatom removal. The total number of moles in the feed was held constant.

In the present study conversion data were determined at 344°C and at fixed hydrogen partial pressure (640 psia), a detailed examination of the effects of process variables on the relative first-order rate constants having been reported earlier (6). Under the above reaction conditions, naphthalene conversion to tetralin approached an equilibrium value of 96.9% (11). Decalin was not produced.

Initial conversion of the various components changed rapidly with time on stream as shown by the example in Figure 1 but reached a stable level after several days on stream. In the time required to reach a "stable" behavior each catalyst was unique. The SiO<sub>2</sub>-promoted catalyst for example exhibited a stable conversion almost immediately. The important observation is contained in Table III, where it is shown that all three CoMo and NiMo catalysts, once stable, were remarkably similar in their behavior. The relative rate constants for conversion of the various NSO compounds never differed by more than a factor of two.

The Mo-only catalyst on the other hand was unique. In the absence of Co or Ni, deN activity was maintained but aromatics saturation and, particularly, deS activity declined markedly. Relative to those observed with a CoMo catalyst (HDS-2), rate constants over Mo-1201T were 0.8, 0.2 and 0.02 for the reaction of quinoline, of naphthalene, and of dibenzothiophene respectively.

Product distributions. The similarity in rate of the CoMo and NiMo catalysts was further reflected in the products of heteroatom removal. Desulfurization reactions require little discussion, all stable CoMo and NiMo catalysts converting benzothiophene to ethylbenzene and dibenzothiophene to biphenyl in over 90% selectivity. Mercaptan sulfur in the products rarely approached 100 ppm indicating that the initial thiophene ring opening, and not thiol hydrogenation, was rate-limiting. This suggestion is supported by the high reactivity of thiophenol (6).

Nitrogen and oxygen removal are more complex reactions, reactions nevertheless common to this group of catalysts. Both indole and quinoline produced the corresponding alkylcyclohexanes in over

Table III

Relative Rate Constant for Conversion700 psig,  $H_2$ /feed = 8, 344°C

	<u>HDS-2</u>	<u>HDS-1441</u>	<u>HDS-3</u>
Rate Constants <sup>a</sup>			
2-Methylnaphthalene <sup>b</sup>	1.0	1.1	1.0
2,3-Dimethylnaphthalene <sup>b</sup>	1.4	1.2	1.3
Dibenzothiophene	3.6	6.3	5.0
Benzothiophene	3.4	6.2	6.0
Indole	0.9	0.9	1.2
Quinoline	1.3	1.7	2.2
2,3-Benzofuran	1.0	1.1	1.0
o-Ethylphenol	1.2	-	-
Dibenzofuran	0.4	0.3	0.3
2-Phenylphenol	1.4	1.4	1.8
p-Cresol	5.2	7.2	-
4-Propylphenol	-	7.6	-

a--Relative to naphthalene; reproducibility,  $\pm 20\%$ 

b--Assumes equilibrium conversion is 97% at 344°C

90% selectivity. In both cases the rate determining step was saturation of the aromatic ring in the o-alkylaniline intermediate, as evidenced both by gas chromatography and by analysis for basic nitrogen, indole being non-basic (9).

Oxygen removal proceeded with similar saturation of the aromatic ring. Benzofuran and the various alkylphenols all yielded alkylcyclohexanes in over 90% selectivity. Phenol analysis of the benzofuran products identified phenol hydrogenation, not furan ring opening, as the rate determining step.

Commercial feeds. Such uniformity of catalyst behavior makes possible an extension of these results to feeds which are not well characterized. The summary in Table IV shows that the hydrogen consumed in removal of any given heteroatom can be estimated without a detailed knowledge of the chemical form of the undesired species. Thus, sulfur removal requires ~110 SCF/bbl of  $H_2$ ; nitrogen, ~650; and oxygen (phenolic as in coal oils), ~400.

In Table V these projections are tested with actual commercial feeds, a resid (high S), a shale oil (high N), and a coal oil (high O). Two comments are appropriate to these data. First, although the quantitative distribution of heteroatom types in these feeds is not known, the relative reactivities of the NSO-species generally reflect the behavior observed with model feeds.

Table IV

Summary of Behavior CoMo and NiMo Catalysts344°C, 700 psig, H<sub>2</sub>/feed = 8

<u>Chemical Species</u>	<u>Relative Rate Constant<sup>a</sup></u>	<u>Moles H<sub>2</sub>/heteroatom</u>	<u>Hydrogen Consumed<sup>b</sup></u>
Sulfides	>50	2	90 SCF
Benzothiophene	5	3	130
Dibenzothiophene	5	2	90
Indole	1.1	6	600
Quinoline	1.7	7	700
p-Alkylphenol	6	4	350
o-Alkylphenol	1.5	4	350
Benzofuran	1.1	6	530

a--Relative to naphthalene, ±20%

b--Hydrogen consumed for each 1.0% heteroatom removed, assuming a change stock density of 1.0g/cc

Table V

Commercial Feed Data for  
CoMo, NiMo, NiW Catalysts

<u>Feed</u>	<u>Arab Light atm. resid<sup>c</sup></u>	<u>Shale Oil, NTU-type (12)</u>	<u>Utah Coal Oil (13)</u>
N, %	0.2	2.0	1.0
S, %	3.6	0.9	0.3
O, %	0.1	a	6.6
Pressure, psig.	700	3000	2500
H <sub>2</sub> circ., SCF/B	9500	6000	15000
Temp., °C	399	375	397
LHSV	2.3	0.5	1.0
deS	80	89	99 <sup>+</sup>
deN	36	65	67
deO	-	-	80
H <sub>2</sub> Consumption, SCF/B	520	1000	2240
Calculated H <sub>2</sub> <sup>b</sup> , SCF/B	370	870	2290

a--Not given

b--From NSO removal and data in Table IV

c--Present work

More important, over 70% of the hydrogen consumed in the processing of these three commercial charge stocks could be accounted for in terms of NSO removal. The remainder is primarily associated with the saturation of polynuclear aromatics.

### Conclusions

Studies with model feed mixtures, mixtures selected to reflect the NSO-content and chemical type distribution found in resids, shale oils, and coal oils, showed that the behavior of a series of CoMo and NiMo catalysts became increasingly similar as the catalysts aged. As is known in the literature (14-18), desulfurization and aromatics hydrogenation activity were substantially reduced in the absence of Co or Ni. Nitrogen removal, however, was little changed.

The results showed that NSO-compounds can be grouped according to reactivity in the order:

Sulfides >> p-alkylphenols > benzothiophenes > quinoline ~  
o-alkylphenols ~ indoles ~ benzofurans ~ naphthalenes > dibenzofurans  
>> mononuclear aromatics.

Examination of the products of hydrogenation indicated that these NSO-compounds fall into two categories in terms of the mechanism of heteroatom removal. Sulfur compounds (sulfides, fused ring thiophenes) were readily cleaved to give H<sub>2</sub>S and alkane or aromatic respectively. With N- and O- species, saturation of any aromatic ring attached to the heteroatom was required prior to C-N or C-O bond scission.

Hydrogen consumption values were determined for NSO- removal from the model compounds, and the values were projected onto the observed behavior of atmospheric resids, coal oils and shale oils.

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FIGURE 1  
 RATE CONSTANTS FOR HYDROGENATION  
 HDS-2, 700 PSIG, 344°C, H<sub>2</sub>/FEED=8

